INFERENCE OF SUBBITUMINOUS COAL STRUCTURE FROM LIQUEFACTION OF WYODAK COAL IN MODEL SOLVENTS*

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Introduction

Knowledge of the structure of coal is necessary if we are to understand coal liquefaction mechanisms and develop novel process concepts. Two important aspects of coal structure are the detailed structure of coal fragments and the nature of the bonds which hold these fragments together (crosslinks), the latter being the most significant to mechanism studies. The most widely accepted model for coal is that reported by Green, et al.[1] Their model consists of a macromolecular three-dimensional network of aromatic "clusters", crosslinked through covalent bonds. In their model, hydrogen bonds play a secondary role, forming only weaker bonds between molecular planes. We shall present evidence in this paper that indicates that hydrogen bonds are the primary bonds holding Wyodak coal fragments together. Evidence also suggest that hydrogen bonds are important in bituminous coal structure,[2,3] but this will not be discussed here.

Information about the nature of the crosslinks in coal has been obtained by observing the interaction of various solvents with coal. Much of the information for the model of coal presented by Green, et al. was obtained from coal swelling experiments.[4] Pampuch[5] demonstrated that the specific interaction between polar liquids and coal is the formation of hydrogen bonds. Also, several recent studies have focused on the depolymerization of coal through direct solvent attack. Larsen, et al.[6] observed depolymerization of three coals in pyridine at 350°C. The exact nature of the coal-solvent interaction was not described. Larsen[7] has also observed depolymerization of Illinois No. 6 coal in aliphatic amine bases at 300°C.

We have studied the interaction behavior of Wyodak subbituminous coal with a variety of model solvents to better understand the nature of the crosslinks in subbituminous coal. We have observed extensive depolymerization of Wyodak coal under low severity conditions, and propose that this depolymerization is the result of disruption of hydrogen bonds in the coal.

Experimental

The data reported below were obtained from batch microreactor runs using Wyodak coal (South Pit Mine) and selected model solvents. The proximate and ultimate analysis of the Wyodak coal are listed in Table 1. The solvents were all used as received from the manufacturer at the stated purity level. The 35 cm^3 microreactors were loaded with an 8 gram sample of a 2/1 solvent to coal mixture. They were then pressurized to 1000 psig with either

hydrogen or nitrogen. A few solvents were used in experiments at higher solvent to coal ratios to see if solvent volatilization was a problem under our conditions. Negligible differences in conversions indicate that at 375°C and a 1000 psig cold charge, solvent volatilization does not lower the solvent to coal ratio enough to alter our results. The microreactors were heated (~3 minutes to reach reaction temperature) in a fluidized sand bath and held at temperature for the specified time. The microreactors were then cooled (~30 seconds for a 200°C quench) in a second fluidized sand bath held at room temperature. Conversion to THF soluble products was obtained by subsampling the whole liquid product from the microreactor, sonicating the sample in THF and then pressure filtering through a 0.2 micron Milipore filter. The filtrate was then analyzed by gel permeation high performance liquid chromatography (HPLC) to observe differences in product distributions.[8] This technique separates the filtrate into high, intermediate, and low molecular weight fractions. These fractions are comparable to the classical preasphaltne (mw ~ 1000), asphaltene (mw ~ 450) and oil (mw ~ 250) fractions obtained by Soxhlet analysis.[8]

Capillary GC analysis was performed on an HP 5800 using a crosslinked 5% phenyl methyl silicone column. The oven temperature was programmed from 100°C to 250°C at 2°C/min. The carrier gas flow rate was 0.5 cm^3/minute. Separated products were identified by a flame ionization detector. Product molecules as large as four and five member ring compounds have been identified by the above GC analysis technique. However, we cannot be certain all THF soluble material passed through the GC column.

Results and Discussion

We began our investigation of Wyodak coal liquefaction in model solvents by conducting experiments in tetrahydroquinoline (THQ). THQ has been observed to enhance coal conversion[3] and also to adduct to coal products.[9] Thus our initial investigation centered on learning if the same characteristic of THQ was responsible for both adduct formation and enhanced conversion. THQ is both a basic nitrogen compound and a hydrogen donor. While its basic characteristic is probably responsible for adduct formation, it is unknown which property contributes most to the enhanced coal conversions observed in THQ.

Figure 1 tabulates the conversions to THF soluble products and the product distributions for Wyodak coal liquefied at 375°C, 20 minutes and 1000 psig H_2 in 1,2,3,4-THQ, quinoline and 5,6,7,8-THQ. Quinoline is a non-hydrogen donor and shows only 23% conversion compared to 80% conversion for 1,2,3,4-THQ and 58% conversion for 5,6,7,8-THQ. In addition to being a non-hydrogen donor, the nitrogen group in quinoline is a teriary amine rather than a secondary amine as in 1,2,3,4-THQ. The 5,6,7,8-THQ should have similar hydrogen donor characteristic as the 1,2,3,4-THQ, but the conversion is much lower. The apparent difference between the two hydrogenated quinolines is that 5,6,7,8-THQ has the same base structure as quinoline.

For comparison, we measured the conversion of Wyodak coal in conventional hydrogen donor solvents, such as tetralin, hexahydropyrene and dihydrophenanthrene. Figure 2 shows the results for these three solvents. While some slight differences are observed, Wyodak conversion to THF soluble products in a good hydrogen donor solvent is 55-60% at these low severity conditions.

This is the same level of conversion that was observed for
5,6,7,8-THQ. Apparently, in 5,6,7,8-THQ only the hydrogen donor
characteristic contributes to the observed conversion, i.e., there
is little contribution from the quinoline type nitrogen structure.
If 5,6,7,8-THQ and 1,2,3,4-THQ are similar hydrogen donors, this
data would suggest that the enhanced conversion observed in
1,2,3,4-THQ is a result of the secondary amine structure.

We next conducted experiments in other basic solvents, which did
not possess hydrogen donor characteristics. This was done to
clarify the role of the basic functionality. Figure 3 shows the
results of three liquefaction runs made in benzofuran, indole and
acridine. We measured a 62% conversion for Wyodak coal liquefied in
indole. Conversions in acridine and benzofuran were quite low. The
high conversion in indole, a non-donor solvent, suggests a strong
interaction between the coal and the basic nitrogen functionality.

The HPLC spectra from the experiments with several basic
nitrogen solvents showed a new peak in the product distribution.
Figure 4 illustrates the appearance of this new molecular weight
peak. We see that a small complex observed with 1,2,3,4-THQ has
grown to be a predominant peak in the molecular weight distribution
of the THF soluble filtrate from Wyodak liquefaction in indole. We
propose that this new peak is the result of an association between
solvent and coal molecules.

Using preparatory-scale HPLC, we isolated samples corresponding
to the new peaks shown in Figure 4. Since the complex peak occurs
near the asphaltene peak, we assumed that the molecular weight of
the isolated samples was approximately 400 amu. Knowing the
elemental composition of indole, Wyodak coal and the isolated
samples, and assuming a uniform elemental distribution for the coal,
allowed us to conclude that the isolated samples contained
approximately 60% indole. This result is consistent with a complex
composed of two indole molecules and one coal molecule. The coal
molecule would have a molecular weight of approximately 160 amu if
the elemental distribution of Wyodak coal is assumed. Such a
complex would have a molecular weight of $\sim$394 amu, in excellent
agreement with the value of $\sim$400 amu observed for the isolated
samples. Thus, our elemental analyses, in conjunction with the
location of the complex peak in the HPLC molecular weight spectrum,
are consistent with a complex composed of two indoles to one $\sim$160
amu coal molecule.

If the indole-coal complex is held together by hydrogen bonds, a
stronger base should displace the indole from the complex. We
refluxed a portion of the complex in dibutylamine at $\sim$150°C for 2
hours. Capillary GC of the complex before and after refluxing
showed striking differences. Before reaction with dibutylamine, the
capillary GC spectrum had only two major peaks at very long
retention time. Following the dibutylamine reflux, a large peak for
free indole was detected and several new peaks appeared at
intermediate retention times. The major peaks previously associated
with the complex were nearly eliminated. This indicates that the
coal-indole complex was bound together through associative hydrogen
bonds.

Indole may participate in a hydrogen bond as either an
electron-acceptor or a electron-donor by virtue of the N-H group.
However, since the unshared electron pair on the nitrogen
participates in the ring resonance, we would expect indole to be a
poor electron donor. We tested the hydrogen bonding role of indole
by liquifying Wyodak in 1-methylindole. With this solvent, in which
the hydrogen on the nitrogen has been replaced by a methyl group,

the solvent cannot act as an electron-acceptor in the formation of
hydrogen bonds. Table 2 lists the conversion results and structural
differences for indole and methylindole. Besides the dramatic
decrease in Wyodak conversion, HPLC spectra indicate very little
complex formation for liquefaction in methylindole. These results
indicate that indole acts primarily as an electron-acceptor in
hydrogen bond formation and that loss of hydrogen bonding ability of
the solvent severely reduces the Wyodak conversion.

The initial experiments were performed under 1000 psig
hydrogen. If indole is solubilizing coal through disruption of
coal-coal hydrogen bonds and formation of coal-indole hydrogen
bonds, then there should be no hydrogen consumption. We measured
the % conversion to THF soluble products for a poor solvent
(quinoline) and indole under both hydrogen and nitrogen pressure.
Conversions for quinoline and indole were virtually the same under
either reacting atomsphere. This suggests little or no hydrogen
consumption from the gas phase, despite the lack of hydrogen
available from either solvent.

At 375°C, there is sufficient thermal energy for some bond
rupture, both covalent bonds and hydrogen bonds. However, under
hydrogen deficient conditions, little conversion can be attributed
to covalent bond rupture as indicated by a measured 20% conversion
in naphthalene. 375°C should be sufficient to break most hydrogen
bonds. Without a strong hydrogen bonding solvent, these bonds would
reassociate as the liquefaction product cools to room temperature.
With indole or another solvent capable of forming hydrogen bonds as
strong or stronger than those present in the coal, these hydrogen
bonding sites in the coal molecule are tied up as coal-indole
bonds. Now as the product cools, reassociation between coal
molecules does not occur and soluble coal-indole complexes are
formed. This mechanism is shown in Figure 5. This type of
mechanism is consistant with our data and suggest that a large
fraction of the Wyodak "clusters" are held together solely by
hydrogen bonds.

Conclusions

We have observed a high conversion of Wyodak coal to THF soluble
products using indole as the liquefaction vehicle. We observed
formation of hydrogen bonded complexes between indole and coal
molecules. We determined that the important structural feature of
indole is the N-H group which acts primarily as an electron-acceptor
in forming hydrogen bonds. Solubilization of Wyodak coal in indole
can best be represented by the pathway presented in Figure 5.

These results for Wyodak liquefaction in indole depict a
liquefaction mechanism based on stabiliztion of hydrogen bonding
sites in the coal. But more importantly, they indicate that a large
fraction of Wyodak coal is crosslinked by hydrogen bonds. The large
fraction of product which is produced as a complex with molecular
weight near the classical asphaltene molecular weight range suggests
that Wyodak coal is composed of clusters with molecular weights
∿160. This structural informaton suggests that a liquefaction
procedure designed to attack the oxygen functionality responsible
for hydrogen bonding in the coal would result in high conversion to
a low molecular weight product.

Table 1. Proximate and Ultimate Analysis of Wyodak Coal
(South Pit Mine)

Proximate*		Ultimate*	
% Moisture	8.45	% Moisture	8.45
% Volatile	40.66	% Carbon	60.62
%Fixed Carbon	41.02	% Hydrogen	4.35
% Ash	9.87	% Nitrogen	0.94
	100.00	% Sulfur	0.68
		% Oxygen (diff)	15.09
		% Ash	9.87
			100.00

* Commercial Testing & Engineering Co., Denver, CO 80239

Table 2. Wyodak liquefaction results at 375°C, 20 minutes
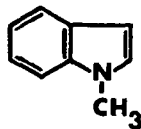and 1000 psig nitrogen.
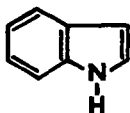
	Indole	Methylindole
% THF Conversion	62%	35%

References

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9. D. C. Cronauer, R. D. McNeil and D. C. Young, Quarterly Progress Report for October-December 1981, DOE/PC/30080-7, June 1982.

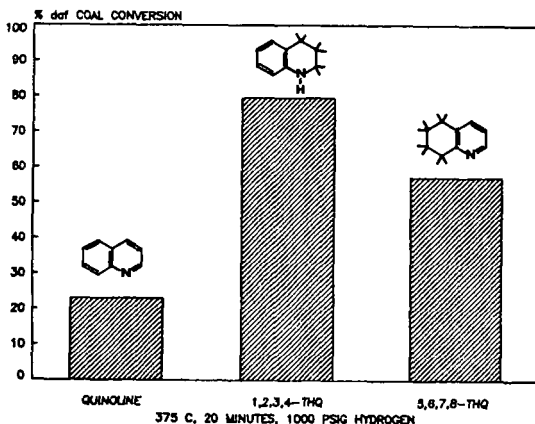Figure 1. Liquefaction results for Wyodak coal in quinoline type solvents.

Figure 2. Liquefaction results for Wyodak
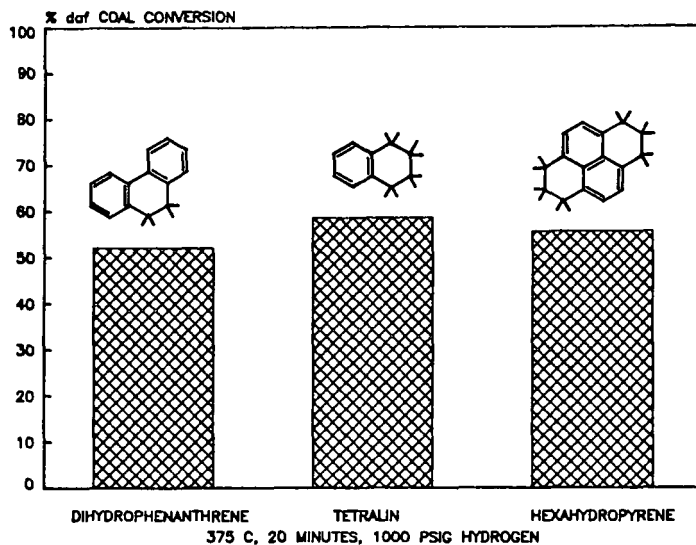coal in hydrogen donor solvents.

% daf COAL CONVERSION

DIHYDROPHENANTHRENE   TETRALIN   HEXAHYDROPYRENE
375 C, 20 MINUTES, 1000 PSIG HYDROGEN

Figure 3. Liquefaction results for Wyodak
coal in other basic solvents.

% daf COAL CONVERSION

BENZOFURAN   INDOLE   ACRIDINE
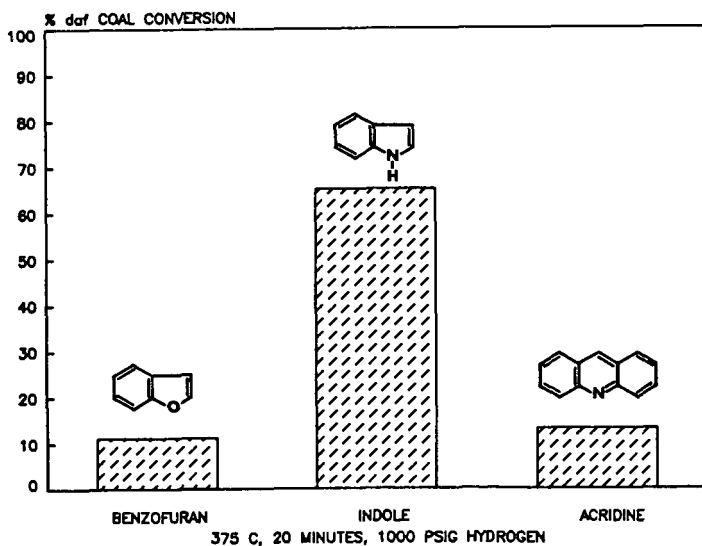375 C, 20 MINUTES, 1000 PSIG HYDROGEN

Figure 4. HPLC spectra of the THF soluble filtrate from microreactor runs.
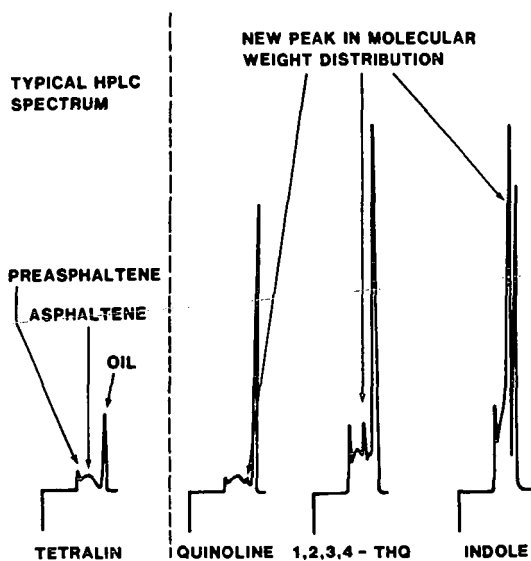

Figure 5. Indole disrupts hydrogen bonded coal matrix to form THF soluble complexes.